Claims

What is claimed is:

1. A method for bonding a first substrate surface to a second substrate surface comprising:

(a) providing a catalyst at the first substrate surface;

(b) providing a metathesizable material between the first substrate surface and the second substrate surface or providing a metathesizable material as a component of the second substrate; and

(c) contacting the catalyst on the first substrate surface with the metathesizable material so that the metathesizable material undergoes a metathesis reaction and bonds the first substrate surface to the second substrate surface.

2. A method according to claim 1 wherein at least one of the substrates comprises an elastomeric material.

3. A method according to claim 2 wherein the elastomeric material is a thermoplastic elastomer.

4. A method according to claim 1 wherein one of the first or second substrates comprises a metallic material and the other first or second substrate comprises an elastomeric material.

5. A method according to claim 4 wherein the metallic material comprises steel and the elastomeric material is selected from natural rubber, polychloroprene, polybutadiene, polyisoprene, styrene-butadiene copolymer rubber, acrylonitrile-butadiene copolymer rubber, ethylene-propylene copolymer rubber, ethylene-propylene-diene terpolymer rubber, butyl rubber, brominated butyl rubber, alkylated chlorosulfonated polyethylene rubber, hydrogenated nitrile rubber, silicone rubber, fluorosilicone rubber, poly(n-butyl acrylate), thermoplastic elastomer and mixtures thereof.

6. A method according to claim 1 wherein the first substrate comprises a tire carcass and the second substrate comprises a tire tread.

7. A method according to claim 1 wherein step (b) comprises applying the metathesizable material to the second substrate surface and step (c) comprises contacting the catalyst on the first substrate surface and the metathesizable material-applied second substrate surface.

8. A method according to claim 1 wherein at least one of the substrates is substantially cured elastomeric material.

9. A method according to claim 4 wherein the elastomeric material is substantially cured.

10. A method according to claim 1 wherein step (c) occurs at room temperature.

11. A method according to claim 1 wherein steps (a)-(c) occur at room temperature.

12. A method according to claim 6 wherein initial bonding in step (c) occurs within one hour.

13. A method according to claim 1 wherein step (a) comprises applying a catalyst onto the first substrate surface.

14. A method according to claim 13 wherein the catalyst is dissolved or mixed into a liquid carrier fluid.

15. A method according to claim 13 wherein the catalyst is included as a component in a multi-component composition.

16. A method according to claim 1 wherein the catalyst is included as a component of the first substrate.

17. A method according to claim 7 wherein the metathesizable material is in the form of a liquid, paste or meltable solid.

18. A method according to claim 7 wherein the metathesizable material is included as a component in a multi-component composition.

19. A method according to claim 1 wherein the metathesizable material is included as a component of the second substrate.

20. A method for bonding a metallic substrate surface to an elastomeric substrate surface comprising:

(a) applying a catalyst to the metallic substrate surface;

(b) applying a metathesizable material to the elastomeric substrate surface; and

(c) bringing the metallic substrate surface and the elastomeric substrate surface together to contact the catalyst and the metathesizable material.

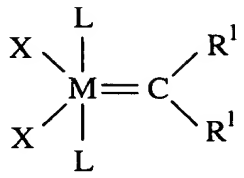
21. A method according to claim 20 wherein step (c) occurs at room temperature.

22. A method according to claim 20 wherein the elastomeric substrate is a substantially cured elastomeric material.

23. A method according to claim 1 wherein the catalyst is selected from at least one of a rhenium compound, ruthenium compound, osmium compound, molybdenum compound, tungsten compound, titanium compound, niobium compound, iridium compound and $MgCl_2$.

24. A method according to claim 23 wherein the catalyst is selected from a ruthenium compound, a molybdenum compound, iridium compound and an osmium compound.

25. A method according to claim 24 wherein the catalyst has a structure represented by



wherein M is Os, Ru or Ir; each R^1 is the same or different and is H, alkenyl, alkynyl, alkyl, aryl, alkaryl, aralkyl, carboxylate, alkoxy, alkenylalkoxy, alkenylaryl, alkynylalkoxy, aryloxy, alkoxycarbonyl, alkylthio, alkylsulfonyl or alkylsulfinyl; X is the same or different and is an anionic ligand group; and L is the same or different and is a neutral electron donor group.

26. A method according to claim 25 wherein X is Cl, Br, I, F, CN, SCN, or N_3; L is $Q(R^2)_a$ wherein Q is P, As, Sb or N; R^2 is H, cycloalkyl, alkyl, aryl, alkoxy, arylate or a heterocyclic ring; and a is 1, 2 or 3; M is Ru; and R^1 is H, phenyl, -CH=C(phenyl)$_2$, -CH=C(CH$_3$)$_2$ or -C(CH$_3$)$_2$(phenyl).

27. A method according to claim 26 wherein the catalyst is a phosphine-substituted ruthenium carbene.

28. A method according to claim 27 wherein the catalyst is bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride.

29. A method according to claim 1 wherein the catalyst is stable in the presence of moisture and oxygen and can initiate polymerization of the metathesizable material upon contact at room temperature.

30. A method according to claim 1 wherein the metathesizable material includes at least one reactive unsaturated functional group.

31. A method according to claim 30 wherein the metathesizable material comprises an olefin.

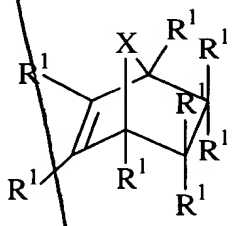
32. A method according to claim 31 wherein the metathesizable material is selected from ethene, α-alkene, acyclic alkene, acyclic diene, acetylene, cyclic alkene, cyclic polyene and mixtures thereof.

33. A method according to claim 32 wherein the metathesizable material comprises a cycloolefin.

34. A method according to claim 33 wherein the metathesizable material is a monomer or oligomer selected from norbornene, cycloalkene, cycloalkadiene, cycloalkatriene, cycloalkatetraene, aromatic-containing cycloolefin and mixtures thereof.

35. A method according to claim 34 wherein the metathesizable material is a norbornene monomer or oligomer.

36. A method according to claim 35 wherein the norbornene has a structure represented by



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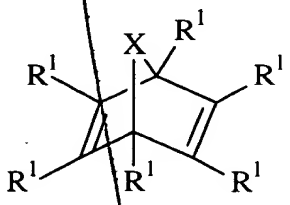

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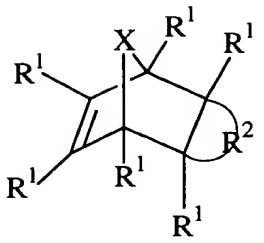

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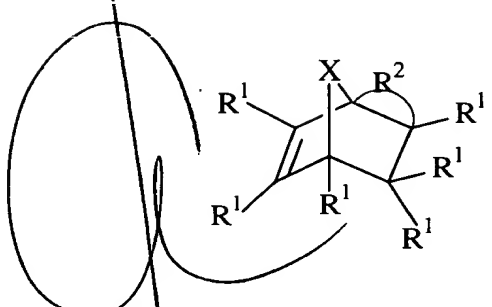


wherein X is CH_2, CHR^3, $C(R^3)_2$, O, S, N-R^3, P-R^3, O=P-R^3, $Si(R^3)_2$, B-R^3 or As-R^3; each R^1 is independently H, CH_2, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano or imido; R^2 is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and R^3 is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy..

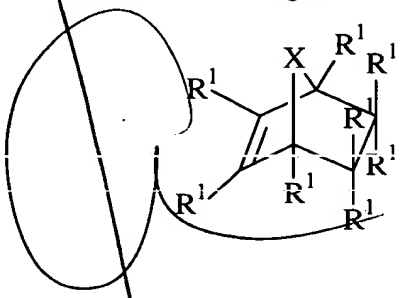
37. A method according to claim 36 wherein the metathesizable material comprises ethylidenenorbornene monomer or oligomer.

38. A method according to claim 1 wherein the metathesizable material comprises liquid ethylidenenorbornene monomer.

39. A method according to claim 1 wherein the catalyst is applied in an aqueous solution or mixture and the metathesizable material is applied in the form of a liquid that is substantially 100 percent reactive.

40. A method according to claim 1 wherein the method is substantially free of the use of volatile organic solvents.

41. A method according to claim 20 wherein the metathesizable material comprises norbornene monomer or oligomer having a structure represented by



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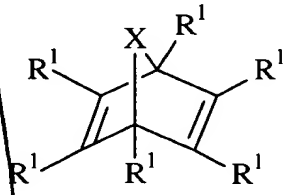

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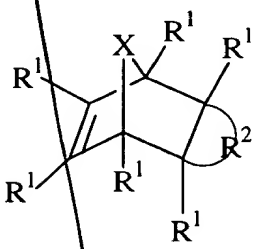

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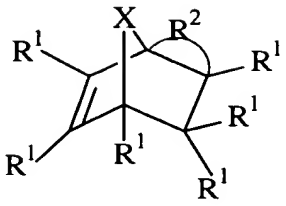


wherein X is CH_2, CHR^3, $C(R^3)_2$, O, S, N-R^3, P-R^3, O=P-R^3, $Si(R^3)_2$, B-R^3 or As-R^3; each R^1 is independently H, CH_2, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano or imido; R^2 is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and R^3 is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy; and the catalyst is selected from a ruthenium compound, a molybdenum compound and an osmium compound.

42. A method according to claim 41 wherein step (c) occurs at room temperature.

43. A method according to claim 1 wherein step (a) comprises applying a ruthenium catalyst in a liquid carrier to the first substrate surface, step (b) comprises applying a metathesizable liquid norbornene monomer to the second substrate surface and step (c) comprises contacting the catalyst-applied first substrate surface and the monomer-applied second substrate surface.

44. A method for bonding a tire tread to a tire carcass comprising:

(a) applying a catalyst to the tire tread or tire carcass;

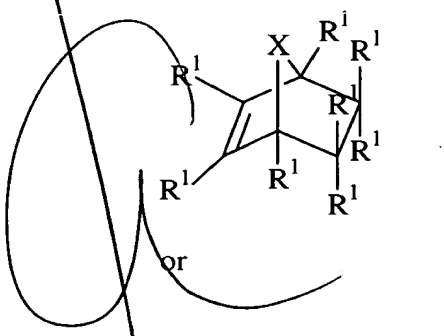
(b) applying a metathesizable material to the tire tread or tire carcass; and

(c) contacting the catalyst-applied tire tread or tire carcass and the metathesizable material-applied tire tread or tire carcass together so that the metathesizable material undergoes a metathesis reaction and bonds the tire tread to the tire carcass.

45. A method according to claim 44 wherein step (c) occurs at room temperature.

46. A method according to claim 44 wherein the tire tread comprises precured retread stock.

47. A method according to claim 44 wherein the metathesizable material comprises norbornene monomer or oligomer having a structure represented by



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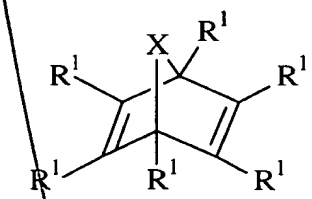

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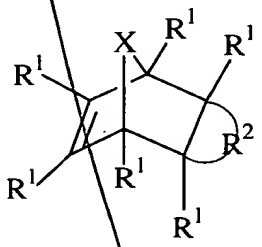

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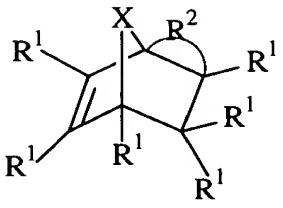


wherein X is CH_2, CHR^3, $C(R^3)_2$, O, S, N-R^3, P-R^3, O=P-R^3, $Si(R^3)_2$, B-R^3 or As-R^3; each R^1 is independently H, CH_2, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano or imido; R^2 is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and R^3 is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy; and the catalyst is selected from a ruthenium compound, a molybdenum compound and an osmium compound.

48. A method according to claim 44 wherein the catalyst is applied to the tire carcass and the metathesizable material is applied to the tire tread.

49. A method according to claim 13 wherein the catalyst is applied so that it is in direct contact with the first substrate surface.

50. A method for adhering a material to a first non-fibrous substrate surface comprising:

(a) providing a catalyst at the first non-fibrous substrate surface; and

(b) contacting the catalyst on the non-fibrous substrate surface with a material that undergoes a metathesis reaction upon contact with the catalyst to adhere the material to the first non-fibrous substrate surface.

51. A method according to claim 50 wherein the catalyst is applied so that it is in direct contact with the first non-fibrous substrate surface.

52. A method according to claim 50 wherein the metathesizable material forms a coating directly on the first non-fibrous substrate surface.

53. A method for providing a coating on a substrate surface comprising:

(a) providing a catalyst at the substrate surface; and

(b) contacting the catalyst on the substrate surface with a material that undergoes a metathesis reaction to form a coating on the substrate surface.

54. A method according to claim 53 wherein the coating is formed directly on the substrate surface.

55. A method according to claim 53 wherein the coating has a thickness that is less than the thickness of the substrate.

56. A method according to claim 53 wherein the substrate comprises a substantially cured elastomeric material.

57. A method according to claim 56 wherein the elastomeric material is a thermoplastic elastomer.

58. A method according to claim 53 wherein step (b) occurs at room temperature.

59. A method according to claim 53 wherein steps (a)-(b) occur at room temperature.

60. A method according to claim 53 wherein step (a) comprises applying a catalyst onto the substrate surface.

61. A method according to claim 60 wherein the catalyst is dissolved or mixed into a liquid carrier fluid.

62. A method according to claim 60 wherein the catalyst is included as a component in a multi-component composition.

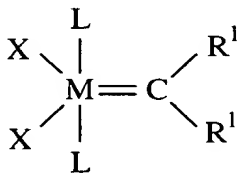
63. A method according to claim 53 wherein the catalyst is included as a component of the substrate.

64. A method according to claim 56 wherein the elastomeric material is selected from natural rubber, polychloroprene, polybutadiene, polyisoprene, styrene-butadiene copolymer rubber, acrylonitrile-butadiene copolymer rubber, ethylene-propylene copolymer rubber, ethylene-propylene-diene terpolymer rubber, butyl rubber, brominated butyl rubber, alkylated chlorosulfonated polyethylene rubber, hydrogenated nitrile rubber, silicone rubber, fluorosilicone rubber, poly(n-butyl acrylate), thermoplastic elastomer and mixtures thereof.

65. A method according to claim 53 wherein the catalyst is selected from at least one of a rhenium compound, ruthenium compound, osmium compound, molybdenum compound, tungsten compound, titanium compound, niobium compound, iridium compound and $MgCl_2$.

66. A method according to claim 65 wherein the catalyst is selected from a ruthenium compound, a molybdenum compound, an iridium compound and an osmium compound.

67. A method according to claim 66 wherein the catalyst has a structure represented by



wherein M is Os, Ru or Ir; each R^1 is the same or different and is H, alkenyl, alkynyl, alkyl, aryl, alkaryl, aralkyl, carboxylate, alkoxy, alkenylalkoxy, alkenylaryl, alkynylalkoxy, aryloxy, alkoxycarbonyl, alkylthio, alkylsulfonyl or alkylsulfinyl; X is the same or different and is an anionic ligand group; and L is the same or different and is a neutral electron donor group.

68. A method according to claim 67 wherein X is Cl, Br, I, F, CN, SCN, or N_3; L is $Q(R^2)_a$ wherein Q is P, As, Sb or N; R^2 is H, cycloalkyl, alkyl, aryl, alkoxy, arylate or a heterocyclic ring; and a is 1, 2 or 3; M is Ru; and R^1 is H, phenyl, -CH=C(phenyl)$_2$, -CH=C(CH$_3$)$_2$ or -C(CH$_3$)$_2$(phenyl).

69. A method according to claim 68 wherein the catalyst is a phosphine-substituted ruthenium carbene.

70. A method according to claim 69 wherein the catalyst is bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride.

Sub B3 71. A method according to claim 53 wherein the catalyst is stable in the presence of moisture and oxygen and can initiate polymerization of the metathesizable material upon contact at room temperature.

Sub C1 72. A method according to claim 55 wherein the metathesizable material includes at least one reactive unsaturated functional group.

73. A method according to claim 72 wherein the metathesizable material comprises an olefin.

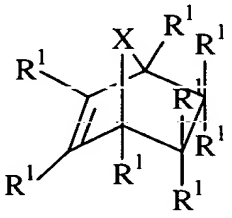
74. A method according to claim 72 wherein the metathesizable material is selected from ethene, α-alkene, acyclic alkene, acyclic diene, acetylene, cyclic alkene and cyclic polyene and mixtures thereof.

Sub D7

75. A method according to claim 53 wherein the metathesizable material comprises a cycloolefin.

76. A method according to claim 75 wherein the metathesizable material is a monomer or oligomer selected from norbornene, cycloalkene, cycloalkadiene, cycloalkatriene, cycloalkatetraene, aromatic-containing cycloolefin and mixtures thereof.

77. A method according to claim 76 wherein the metathesizable material comprises a norbornene having a structure represented by



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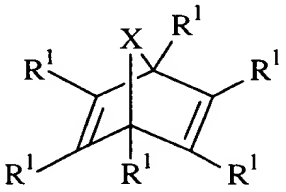

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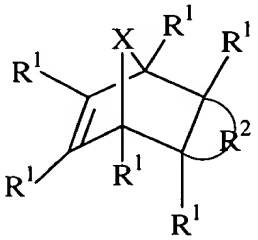

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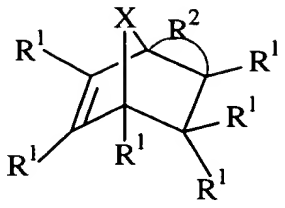


wherein X is CH_2, CHR^3, $C(R^3)_2$, O, S, N-R^3, P-R^3, O=P-R^3, $Si(R^3)_2$, B-R^3 or As-R^3; each R^1 is independently H, CH_2, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano or imido; R^2 is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and R^3 is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy.

78. A method according to claim 77 wherein the metathesizable material comprises ethylidenenorbornene monomer or oligomer.

79. A method according to claim 53 wherein the metathesizable material is in the form of a liquid.

80. A method according to claim 53 wherein the metathesizable material is a component of a multi-component composition.

81. A method according to claim 53 wherein the catalyst is applied in the form of an aqueous solution or mixture and the metathesizable material is applied in the form of a liquid that is substantially 100 percent reactive.

82. A method according to claim 53 wherein the method is substantially free of the use of volatile organic solvents.

83. A method according to claim 53 wherein step (a) comprises applying a ruthenium catalyst in a liquid carrier to the substrate surface and step (b) comprises

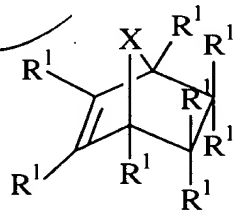
applying a metathesizable liquid norbornene monomer to the catalyst-applied substrate surface.

84. A manufactured article produced by the method of claim 1.

85. A manufactured article that includes a first substrate surface, a second substrate surface and an adhesive layer interposed therebetween, wherein the first substrate surface comprises an elastomeric material and the adhesive layer comprises a metathesis polymer.

86. A manufactured article according to claim 85 wherein the second substrate surface comprises a metallic material.

87. A manufactured article according to claim 85 wherein the metathesis polymer is produced from a norbornene monomer having a structure represented by



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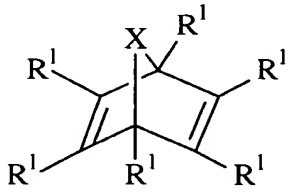

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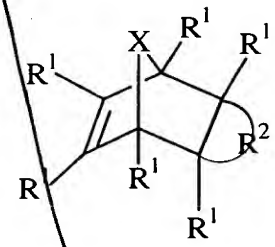

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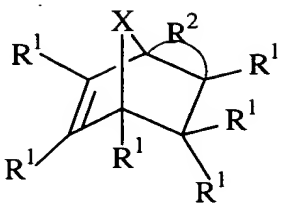


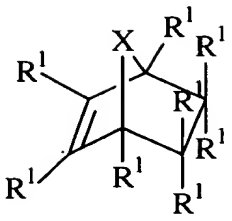
wherein X is CH_2, CHR^3, $C(R^3)_2$, O, S, N-R^3, P-R^3, O=P-R^3, $Si(R^3)_2$, B-R^3 or As-R^3; each R^1 is independently H, CH_2, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano or imido; R^2 is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and R^3 is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy.

88. A manufactured article according to claim 87 wherein the norbornene monomer comprises ethylidenenorbornene.

89. A manufactured article according to claim 85 wherein the elastomeric material comprises a thermoplastic elastomer.

90. A tire laminate comprising a tire carcass have an outer periphery surface, a tire tread having a bonding surface, and a metathesis polymer adhesive layer between the outer periphery surface of the tire carcass and the bonding surface of the tire tread.

91. A tire laminate according to claim 90 wherein the metathesis polymer is produced from a norbornene monomer having a structure represented by



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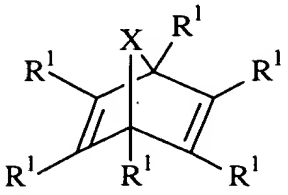

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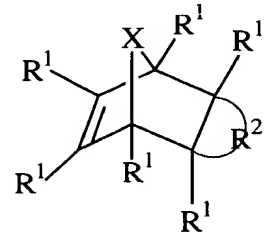
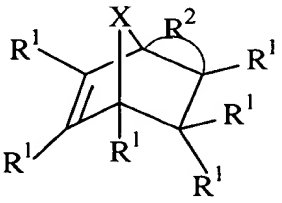


or



wherein X is CH_2, CHR^3, $C(R^3)_2$, O, S, N-R^3, P-R^3, O=P-R^3, $Si(R^3)_2$, B-R^3 or As-R^3; each R^1 is independently H, CH_2, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano

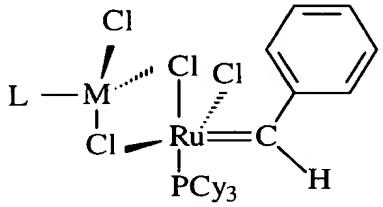
or imido; R^2 is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and R^3 is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy.

92. A manufactured article according to claim 91 wherein the norbornene monomer comprises ethylidenenorbornene.

93. A method according to claim 53 wherein step (b) comprises contacting the substrate surface multiple times with the metathesizable material so as to form multiple coating layers.

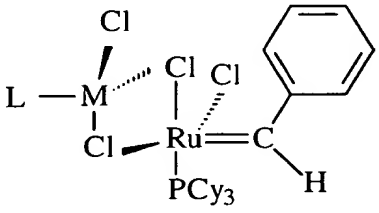
94. A method according to claim 93 wherein an active amount of catalyst remains on the substrate surface after each successive coating sufficient to polymerize the subsequent application of the metathesizable material.

95. A method according to claim 24 wherein the catalyst comprises a bimetallic catalyst having a structure represented by



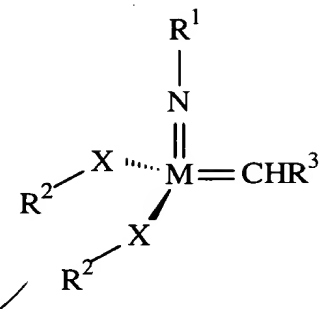
wherein L is p-cymene or 1,3-di-t-butylcyclopentadiene and M is Ru, Os or Rh.

96. A method according to claim 66 wherein the catalyst comprises a bimetallic catalyst having a structure represented by



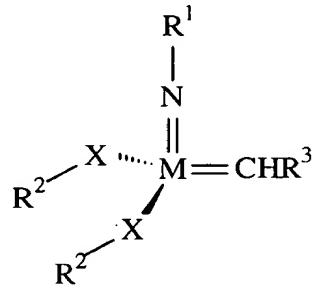
wherein L is p-cymene or 1,3-di-t-butylcyclopentadiene and M is Ru, Os or Rh.

97. A method according to claim 24 wherein the catalyst has a structure represented by



wherein M is Mo or W; X is O or S; R^1 is an alkyl, aryl, aralkyl, alkaryl, haloalkyl, haloaryl, haloaralkyl, or a silicon-containing analog thereof; R^2 are each individually the same or different and are an alkyl, aryl, aralkyl, alkaryl, haloalkyl, haloaryl, haloaralkyl, or together form a heterocyclic or cycloalkyl ring; and R^3 is alkyl, aryl, aralkyl or alkaryl.

98. A method according to claim 66 wherein the catalyst has a structure represented by



wherein M is Mo or W; X is O or S; R^1 is an alkyl, aryl, aralkyl, alkaryl, haloalkyl, haloaryl, haloaralkyl, or a silicon-containing analog thereof; R^2 are each individually the same or different and are an alkyl, aryl, aralkyl, alkaryl, haloalkyl, haloaryl, haloaralkyl, or together form a heterocyclic or cycloalkyl ring; and R^3 is alkyl, aryl, aralkyl or alkaryl.

add C47
add D7
add E37